LED-Assisted Degradation of Aromatic Organics Using Cu_2O Photocatalysts

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ABSTRACT

In this work, we successfully synthesized rhombic dodecahedral Cu_2O nanocrystals with a size of 300 – 400 nm using a facile hydrothermal method. The as-prepared photocatalyst with narrow bandgap is activated using low power visible LED light sources and shows high efficiency in degrading aromatic organic compounds including toluene and chlorobenzene. The OH substitution leads to oxidation/ionization potential drops while the nature of the p-type Cu_2O contributes to an effective single electron transfer reaction.

INTRODUCTION

Aromatic organic compounds widely exist in industrial wastewater at high toxicity levels, causing serious ecological pollution. Conventional biological treatment methods are not suitable for industrial wastewater because of the high concentration of aromatic compounds. Photocatalysis could potentially serve as a clean and low-cost technology for industrial wastewater treatment and the degradation of various categories of organics have been reported [1,2,3]. Conventional photocatalyst materials e.g. TiO_2, needs to be activated by UV light in view of its large bandgap thus limiting its application. Cuprous oxide (Cu_2O), as a typical p-type semiconductor with a narrow band gap of 2-2.2 eV, can be activated by visible light. The Cu_2O photocatalyst has attracted much research interests and its morphology-dependent properties have received considerable attention. A large number of Cu_2O structures have been reported [4,5,6,7]. Rhombic dodecahedral structure with all active (110) facets has been reported to show higher photocatalytic reactivity than other architectures [8]. Dyes including methyl orange, methyl blue, Congo red, etc. have been frequently used for photocatalysis experiments [9,10,11] while only sporadic works have been published on the degradation of aromatic organics [12]. The degradation of aromatic organics is reported to be initiated by single-electron transfer (SET) chemistry and hydroxyl-like chemistry [13], while the pathway and capability of degrading aromatic compounds using Cu_2O photocatalyst is still unclear.

In this work, we successfully synthesized uniform 300 - 400 nm rhombic dodecahedral Cu_2O nanocrystals through a hydrothermal method. The as-prepared nanocrystals were characterized using SEM, TEM, UV-vis spectra, XRD and XPS techniques. The ability to degrade aromatic organics were tested using chlorobenzene and toluene solutions. The degradation mechanism is studied using the GC/MS system. The as-prepared Cu_2O photocatalyst has demonstrated high reactivity towards the degradation of aromatic organics and the potential to serve as a green strategy for industrial wastewater treatment.

EXPERIMENT

Material

Copper(II) chloride (97%), hydroxylamine hydrochloride (99%), and SDS (98.5%) were purchased from Sigma Aldrich. Sodium hydroxide (98%) was purchased from Fisher brand. All chemicals were used as received without further purification.

Synthesis of rhombic dodecahedral Cu_2O nanocrystals

67 mg $CuCl_2$ and 1 g SDS were dispersed in 65 mL deionized water. The solution was placed in a water bath at 35 °C with vigorous stirring for 10 min. 10 mL of 0.2 M NaOH and 25 mL of 1.0 M $NH_2OH{\cdot}HCl$ were introduced. The solution was stirred for 30 s and kept in the water bath for 1 h. The products were centrifuged at 5000 rpm for 4 min, and the precipitate was washed and centrifuged twice using 50 mL of water and ethanol. The resulting products were dried in the oven at 60 °C for 12 h.

Nanocrystal characterization

The morphologies of synthesized nanocrystals were studied using LEO GEMINI 1530VP scanning electron microscopy (SEM) at 8 kV and FEI Tecnai G2 20 transmission electron microscopy (TEM) at 200 kV. Ultraviolet-visible (UV-vis) absorption spectra was measured using a UniCam UV/VIS spectrometer v.2. X-ray diffraction (XRD) patterns were recorded by a Bruker D8 Advance diffractometer with Cu K α radiation. X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI5000VersaProbe II scanning XPS microscope.

Photocatalysis experiment

Visible light LEDs were used as the light source. The spectra of the light source was measured using a Labsphere CDS-600 spectrometer. The photocatalysis experiment was carried out in a homemade quartz immersion reactor with a volume of 330 mL at room temperature. One portion of pristine Cu_2O photocatalysts was dispersed in 300 mL toluene or chlorobenzene solution. The categories and concentrations of organic compounds were studied using a Thermo Scientific DSQ II GC/MS system.

DISCUSSION

SEM and TEM images viewed along [100], [110] and [111] directions of the as-prepared rhombic dodecahedral Cu_2O nanocrystals are presented in Figure 1. Each rhombic dodecahedral Cu_2O nanocrystal with the size of 300 – 400 nm has 12 (110) facet.

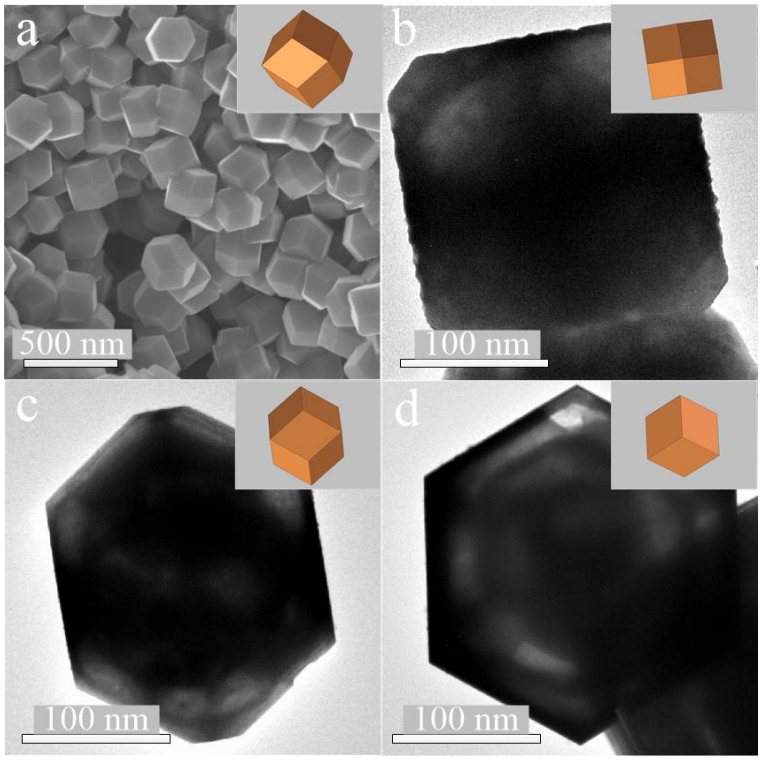

Figure 1. (a) SEM image of rhombic dodecahedral Cu_2O nanocrystal: TEM images viewed along (b) [100], (c) [110], and (d) [111] directions.

The spectra of visible LED light sources is shown in Figure 2a. No UV component (wavelength < 400 nm) is detected and the peak is located at 455 nm as shown in Figure 2a. The absorption spectra of as-prepared rhombic dodecahedral Cu_2O nanocrystal has an absorption peak that is consistent with the intensity peak of the LED light source, indicating that the rhombic dodecahedral Cu_2O nanocrystal is able to maximally take advantage of the LED spectra. The characteristic light-scattering feature from 500 to 1000 nm due to large particle size can be observed.

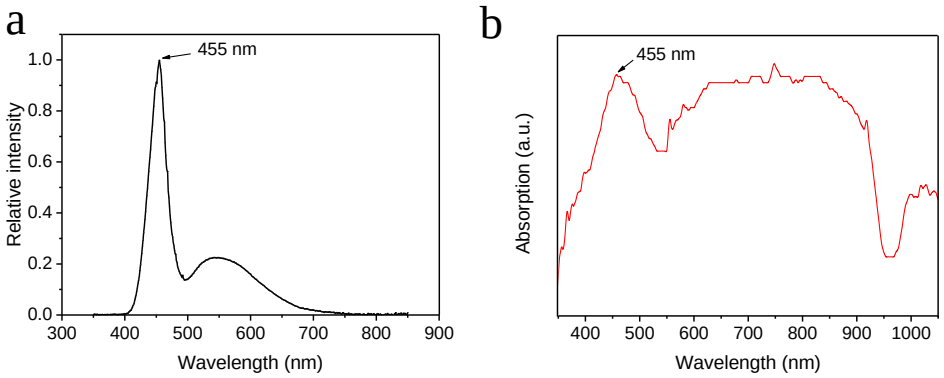

Figure 2. (a) Spectra of visible LED light source; (b) UV-vis absorption of Cu_2O nanocrystal.

The purity of as-obtained products were detected using XRD and XPS technologies and the patterns are demonstrated in Figure 3. The XRD pattern of rhombic dodecahedral Cu_2O

nanocrystal matches the standard Cu_2O XRD pattern, denoting high phase purity. The peaks of Cu $2p_{1/2}$(952.28 eV) and Cu $2p_{3/2}$ (932.38 eV) in Figure 3b implies the +1 chemical valence of Cu in the product.

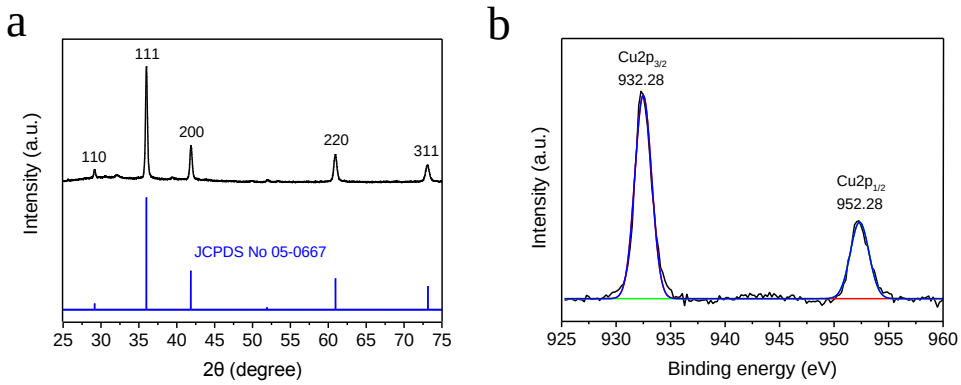

Figure 3. (a) XRD, and (b) XPS patterns of Cu_2O nanocrystal.

The photocatalytic degradation performance of chlorobenzene and toluene are presented in Figure 4. For the photocatalysis experiment of chlorobenzene, one portion of as-prepared Cu_2O photocatalyst was dispersed in 300 mL 6 mg/L chlorobenzene solution.

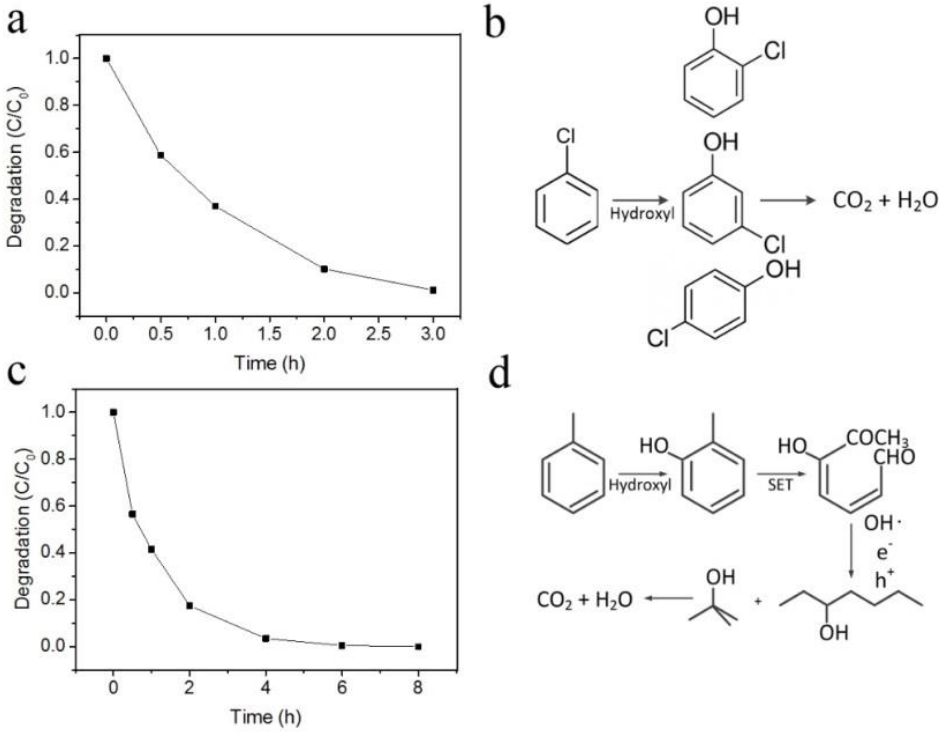

Figure 4. Degradation of (a) chlorobenzene and (b) degradation mechanism; Degradation of (c) toluene and (d) degradation mechanism.

After 3 h of photocatalytic degradation under the irradiation of LED light source, 98.8 % of chlorobenzene is removed as shown in Figure 4a. The intermediate products are analysed

using Thermo Scientific DSQ II GC/MS system and chlorophenol is detected during the photocatalytic process. The hydroxyl-like chemistry leads to the formation of chlorophenol and the oxidation/ionization drop of aromatic organics. No organics were detected in the end, denoting the final products are carbon dioxide and water. 300 mL of 2 mg/L toluene solution was also used for the photocatalysis experiments. 100 % of toluene is degraded after 8 h of photocatalytic reaction as shown in Figure 4c. OH substitution takes place at the first stage and lowers the oxidation/ionization potential. The ring-opening reaction is initiated by SET chemistry. Cu_2O as a p-type semiconductor with majority hole carriers benefits SET reactions with the adsorbed aromatic organics. The by-products further react with the electrons, holes and hydroxyl species to form smaller molecules e.g. 3-heptanol and 2-methyl-2-propanol, and finally carbon dioxide and water. The as-prepared Cu_2O photocatalyst has also demonstrated its ability to degrade a wide range of aromatic organics effectively as in our previous work [14].

CONCLUSIONS

Uniform 300 – 400 nm rhombic dodecahedral Cu_2O nanocrystals have been successfully synthesized using a facile hydrothermal method. The as-prepared Cu_2O is able to be activated by visible LED light source and its p-type nature benefits SET chemistry, leading to effective ring-opening reactions with aromatic organics. Rhombic dodecahedral Cu_2O nanocrystal is able to degrade chlorobenzene, toluene and other aromatic organics effectively, and demonstrates its potential as a green, economic method for industrial wastewater treatment.

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